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XI.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

BY WOLCOTT GIBBS, M. D.,

Rumford Professor Emeritus in Harvard University.

Presented August 1, 1894.

(Continued from Vol. XXI., page 128.)

PLATINO-TUNGSTATES.

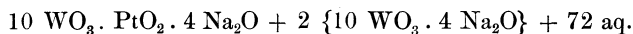
IN a notice of these and corresponding compounds of molybdenum published some years since,* and intended to be only preliminary, I pointed out the analogy between them and the silico-tungstates of Marignac. The notice in question requires correction in several particulars, and I shall here give the results of a more complete investigation, conducted with better facilities for work and with a much wider acquaintance with the whole class of complex acids.

Platinic hydrate, like silicic hydrate, dissolves when boiled with solutions of alkaline tungstates belonging to the meta-tungstic series. Platino-tungstates are formed under these circumstances, but various conditions require to be considered. In general I have been accustomed to prepare the hydrate $\text{Pt}(\text{OH})_4$ by Frémy's method, that is, by boiling a solution of platinic chloride with a large excess of sodic hydrate for some time and then adding acetic acid in small excess, when the platinic hydrate separates as a pale buff-yellow slimy compound to be washed by repeated decantation with cold water. When the last portions of saline matter have been removed the wash-water becomes turbid and settles only after very long standing. The hydrate obtained in this way sometimes dissolves very readily in hot solutions of alkaline tungstates, sometimes only after long boiling, and sometimes is almost insoluble. The process is therefore an uncertain one at best. The platino-tungstates formed have a yellow or orange-yellow color and in many cases crystallize well. By the process which I have given it is usually difficult to obtain perfectly saturated compounds

* *Berichte der deutschen chemischen Gesellschaft*, X. 1384. 1877.

unless a rather large excess of platinic hydrate is employed. When this is the case a greater or less quantity of a deep orange-red solution is sometimes formed, which on standing deposits a dark tarry mass in case the sodic tungstate is employed. In place of sodic hydrate I have also used baric hydrate in preparing a soluble form of the platinum compound, but in this case also the platinic hydrate, according to varying conditions, varied very much in solubility.

When platinic hydrate is boiled with a solution of 10 : 4 sodic tungstate the latter being in large excess, yellow solutions are sometimes formed which on evaporation and standing yield large crystalline masses with a fine yellow color and strong lustre. These crystals consist essentially of the 10 : 4 sodic salt, $10 \text{ WO}_3 \cdot 4 \text{ Na}_2\text{O} + 23 \text{ aq.}$, but they contain a greater or less proportion of a platinic compound which — water of crystallization apart — has probably the formula $10 \text{ WO}_3 \cdot \text{PtO}_2 \cdot 4 \text{ Na}_2\text{O}$, and which appears to be isomorphous with the tungstate. A compound of this kind gave on analysis figures which corresponded very closely with the formula,



We may have here a combination of two isomorphous salts, having respectively the formulæ, $10 \text{ WO}_3 \cdot \text{PtO}_2 \cdot 4 \text{ Na}_2\text{O} + 26 \text{ aq.}$, and $10 \text{ WO}_3 \cdot 4 \text{ Na}_2\text{O} + 23 \text{ aq.}$ The analyses of two different preparations of the salts correspond very closely.

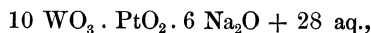
The difficulty of obtaining definite compounds by direct solution of platinic hydrate led me to another method, which may be used with much advantage. Pure crystallized sodic tungstate is to be dissolved in water, a rather large excess of sodic hydrate added, and a neutral or nearly neutral solution of platinic chloride added to the boiling solution in small portions at a time. Platinic hydrate is formed and instantly dissolved. The chloride is to be added until a distinct excess of $\text{Pt}(\text{OH})_4$ is present. Acetic acid is then to be added in small excess. Alcohol then often throws down a dark tarry mass which contains one or more saturated platino-tungstates. When the proportion of platinic chloride necessary happens to be exact, a beautiful orange-colored clear solution is formed which on cooling or evaporation deposits an abundance of beautiful yellow needles or prisms easily purified by recrystallization. By this process a definite salt may be prepared in a very short time and in large quantity. Different salts are, however, formed under different conditions, and further investigations must show whether it is possible by using definite quantities of platinic chloride and of sodic tungstate to obtain uniform results as regards the constitu-

tion of the salt formed. It is indispensable to employ pure platonic chloride or chlorplatينات. Even traces of iridium give a greenish tint to the platino-tungstates formed, a fact which misled me in my earlier experiments. Contrary to my preliminary statement, I now find, on more prolonged study, no isomeric platino-tungstates.

10:1:6 *Sodic Platino-tungstate*. 12:5 sodic tungstate very readily dissolves platonic hydrate in its soluble form, and gives a fine deep orange-colored solution which on standing yields a mass of ill defined dull orange crystals. These may be redissolved, recrystallized, and dried on woollen paper. Of these crystals:

1.1460 grams gave 0.8430 gram Pt + WO ₃	= 73.56 per cent.
1.1806 grams gave 0.0686 gram Pt + WO ₃	= 73.57 “
1.1806 grams gave 0.0706 gram platinum	= 5.98 “
1.1460 grams gave 0.8695 gram platinum	= 6.06 “
1.8770 grams gave 0.7774 gram WO ₃	= 67.83 “
0.8770 gram lost on ignition 0.1397 gram oxygen and water,	
= 15.93 per cent.	

The analyses lead to the formula,



which requires:—

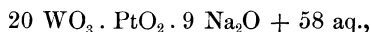
		Calculated.		Mean.		Found.	
10 WO ₃	2320	67.79	} 74.40	67.65	} 74.65	67.56	67.83 67.57
PtO ₂	226.5	6.61		7.00		6.96	7.05
6 Na ₂ O	372	10.87	} 25.60			10.51	} 25.45
28 H ₂ O	504	14.73				14.94	
		3422.5	100.00				

The soda being estimated by difference. It is remarkable that this salt contains six molecules of base instead of four, all known silico-tungstates being tetrabasic. The solution of this salt when shaken with a solution of potassic bromide gives an amorphous pasty mass with a deep orange-red color. In the analysis of this class of compounds it is best to determine the platinum by ignition with sodic carbonate. On treatment of the fused mass with water, the platinum remains as metal, and the tungsten may then be determined in the filtrate in the usual manner. Nearly all the analyses were made in this way, sodic oxide being determined by difference. In some cases, however, tungstic and platonic oxides were precipitated together by mercurous nitrate and mercuric oxide.

20:1:9 *Sodic Platino-tungstate*. In one experiment in which I boiled a portion of pure sodic tungstate with a considerable excess of sodic hydrate, and added to the boiling solution chlorplatinic acid (PtCl_6H_2) in small portions at a time, a fine yellow solution was formed, after addition of an excess of acetic acid, which soon deposited a mass of topaz-yellow crystals. This could be redissolved and re-crystallized without decomposition. The mother liquor appeared to contain one or two other salts. Of this salt:

- (1) 1.4847 grams lost on ignition 0.2453 gram = 16.52% $\text{O} + \text{H}_2\text{O}$.
- (4) 1.4154 grams lost on ignition 0.2349 gram = 16.61% $\text{O} + \text{H}_2\text{O}$.
- (2) 1.4847 grams gave 0.0466 gram platinum = 3.73% PtO_2 .
- (3) 1.0976 grams gave 0.0345 gram platinum = 3.65% PtO_2 .
- (5) { 1.4154 grams gave 1.0467 grams platinum = 3.83%.
- { 1.4154 grams gave 1.0129 grams WO_3 = 71.57%.
- (6) 1.4847 grams gave 1.0619 grams WO_3 = 71.50%.

The analyses lead to the formula,



which requires:

		Calculated.	Mean.	Found.		
20 WO_3	4640	71.73	71.53	71.57	71.50	
PtO_2	226.5	3.50	3.74	3.73	3.65	3.83
9 Na_2O	558	8.63	8.68	8.67		
58 H_2O	1044	16.14	16.05	16.00	16.09	
	6468.5	100.00				

The solution of this salt has a strongly acid reaction with litmus. It gives with ammoniac chloride beautiful colorless scaly crystals, slightly soluble in cold but soluble in boiling water, exactly resembling in appearance the sodio-ammoniac tungstate, $12 \text{ WO}_3 \cdot \text{Na}_2\text{O} \cdot 4 (\text{NH}_4)_2\text{O}$, and containing no platinum. This reaction seems to support the view that the compound is a double salt, and we may perhaps assume that it is represented by the formula,



The principal reactions of this salt are as follows:—

With AgNO_3 a white fine grained crystalline precipitate settling slowly.

With TiNO_3 a similar precipitate in rather coarser grains.

With SO_4Cu a very pale blue or bluish white fine grained precipitate.

With HgNO_3 a bright yellow amorphous precipitate.

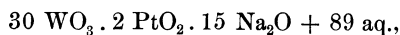
With $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ a pale buff precipitate quickly becoming crystalline in leaves.

A quantity of this platino-tungstate was precipitated by a solution of mercurous nitrate. The fine yellow mercurous salt was well washed and then decomposed by dilute chlorhydric acid, the platino-tungstate being in very small excess. The clear yellow filtrate on spontaneous evaporation deposited a pale yellow substance which may prove to be the corresponding acid.

30 : 2 : 15 *Sodic Platino-tungstate*. This salt was obtained under the same conditions as the last, and formed granular efflorescent dull yellowish crystals readily soluble in water. Of this salt :

- { 1.3231 grams gave 0.9787 gram $\text{WO}_3 + \text{Pt}$ = 73.97 per cent.
- { 1.3231 grams gave 0.0510 gram platinum = 4.49 per cent PtO_2 .
- 1.0144 grams gave 0.0410 gram platinum = 4.70 per cent PtO_2 .
- 1.5776 grams lost on ignition with WO_4Na_2 0.2657 gram $\text{O} + \text{H}_2\text{O}$
= 16.71 per cent.
- 1.5776 grams gave 1.1059 grams WO_3 = 70.06 per cent.
- 1.3231 grams gave 0.9271 gram WO_3 = 70.03 per cent.

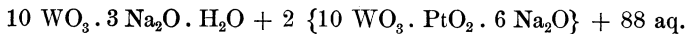
The analyses lead to the formula,



which requires :

		Calculated.	Found.	
30 WO_3	6960	69.98	70.03	70.06
2 PtO_2	453	4.56	4.49	4.70
15 Na_2O	930	9.35	9.24	
89 H_2O	1602	16.11	16.18	
	9945			

A solution of this salt also gives white scaly crystals with potassic and ammoniac salts. It gives a white flocky precipitate with baric chloride, and a pale yellow flocky crystalline precipitate with mercurous nitrate. The compound is probably, like the last described, a double salt and may have the formula,

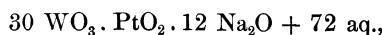


The solution of the salt is acid to litmus. Analysis by Dr. Morris Loeb.

30 : 1 : 12 *Sodic Platino-tungstate*. I obtained this salt by boiling platinic hydrate with 10 : 4 sodic tungstate for some time in a platinum vessel. It formed very large masses of honey-yellow heavy crystals, very easily soluble in water. Of this salt :

1.1441 grams lost on gentle heating 0.1583 gram water = 13.84%.
 0.9383 gram lost on gentle heating 0.1313 gram water = 13.99%.
 1.8069 grams gave 1.4033 grams $\text{WO}_3 + \text{Pt}$ = 77.66%.
 0.8809 gram gave 0.6847 gram $\text{WO}_3 + \text{Pt}$ = 77.72%.
 * ——— gram gave ——— gram platinum = 2.46% PtO_2 .

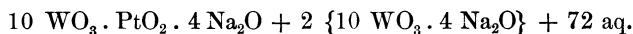
The analyses agree with the formula,



which requires:

		Calculated.	Found.	
30 WO_3	6960	75.44	75.53	75.43
PtO_2	226.5	2.45		2.46
12 Na_2O	744	8.06		8.15
72 H_2O	1296	14.05	13.84	13.99
	9226.5	100.00		

In the analyses the water was determined by heating in an air-bath, and not by ignition. No correction for oxygen of PtO_2 is therefore applied. The solution of the salt gives the characteristic white scaly crystals with NH_4Cl and KCl , and as in the last two cases we may safely assume that the compound is a double salt. The most probable formula considering the mode of formation is,



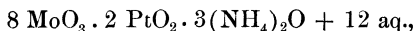
From the above it appears that, strictly speaking, none of the compounds described correspond to the silico-tungstates of Marignac, all of which appear to contain four molecules of basic oxide. Such platinum compounds may, however, exist in combination, as seems to be shown in the salts last described.

The other metals of the platinum group will probably be found to form similar compounds. Want of material has prevented a careful study of the subject, but a number of qualitative tests made with small quantities of salts of iridium, ruthenium, palladium, and osmium appeared to show clearly that these metals also form compounds with tungstic and molybdic oxides analogous to those of platinum.

8:2:3 *Platino-molybdate of Ammonium*. When freshly prepared sodic platinate $\text{Na}_2\text{O} \cdot 3 \text{ PtO}_2$ is boiled with a solution of 14:6 ammonic molybdate, it readily dissolves to an orange-yellow liquid, which after a time deposits beautiful lemon-yellow crystals, which may be easily purified by recrystallization. The salt dissolves rather easily in

* The data of this analysis were accidentally lost.

cold, and very readily in hot water. The solution gives with argentic nitrate a pale yellow flocky precipitate which becomes crystalline on standing. With mercurous, mercuric, and thallos nitrates it gives pale yellow flocky precipitates not distinctly crystalline and settling quickly. With nitrate of croceo-cobalt the solution gives a beautiful bright yellow crystalline salt. The formula of the ammonium salt is,



as the following analyses show :

1.7831 grams gave 0.3554 gram Pt	= 19.94% = 23.21% PtO ₂ .
0.5425 gram gave 0.1075 gram Pt	= 19.82% = 23.09% PtO ₂ .
0.4354 gram gave 0.0868 gram Pt	= 19.92% = 23.15% PtO ₂ .
1.0407 grams gave 0.0535 gram NH ₃	= 5.14%.
0.5149 gram gave 0.0405 gram NH ₃	= 5.14%.
0.5878 gram gave 0.0459 gram NH ₃	= 5.14%.
1.2015 grams lost on ignition with WO ₄ Na ₂	0.2663 gram 22.17% H ₂ O + NH ₃ + O.
0.8368 gram lost on ignition with WO ₄	0.1876 gram 22.42% H ₂ O + NH ₃ + O.

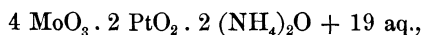
		Calculated.	Mean.		Found.	
8 MoO ₃	1152	58.27	57.83			
2 PtO ₂	453	22.91	23.15	23.21	23.09	23.15
6 NH ₃	102	5.16	5.14	5.14	5.14	5.14
15 H ₂ O	270	13.66	13.88	13.76	14.01	
	1977	100.00				

Other salts of this series may be prepared from the ammonium salt by precipitating its solution with mercurous nitrate and decomposing the well washed mercurous salt by solutions of the chlorides of other metals.

4 : 2 : 2 Platino-molybdate of Ammonium. The solution from which the yellow ammonium salt first described separated by crystallization gave on evaporation a dark colored liquid over a heavy oily deep brown-red substance. This last was washed with a little ice-cold water and gradually dried to a transparent dark brown-red mass which broke up into clean sharp brilliant fragments. Of this salt :

{	0.4502 gram lost on careful heating	0.1297 gram = 28.81% H ₂ O
	+ NH ₃ + O.	
	0.4502 gram gave 0.1226 gram platinum	= 31.63% PtO ₂ .
	0.5398 gram gave 0.0402 gram (NH ₄) ₂ O	= 4.91% NH ₃ .
	0.4917 gram gave 0.0369 gram (NH ₄) ₂ O	= 4.87% NH ₃ .

The analyses lead to the formula,

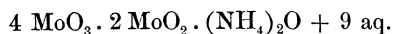


which requires :

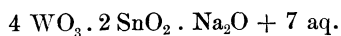
		Calculated.	Found.	
4 MoO ₃	576	40.03	39.56	
2 PtO ₂	453	31.48	31.63	
4 NH ₃	68	4.72	4.91	4.87
19 H ₂ O	342	23.77	23.97	
	1439	100.00		

As in the last case the molybdic oxide is estimated by difference which in the present state of our knowledge of analysis is the most accurate method. The salt can hardly have been absolutely pure. Water decomposes it and gives an opaque buff-yellow compound which I have not examined. It will be seen from the above that the platino-molybdates described do not correspond in general composition with the only silico-molybdates known in which the ratio of molybdic to silicic oxide is as 12 : 1.

Rammelsberg* has described a molybdate of the dioxide and ammonium which has the formula,



In endeavoring to prepare a class of stanno-tungstates I obtained a sodium salt the solution of which gave on evaporation a hard nearly colorless glassy mass. This gave on analysis results which did not correspond very well, but the mean of several led to the formula,



The compound deserves further study, and is not without interest in connection with the two salts noticed above.

60 : 1 : 10 *Platino-molybdate of Potassium*. This salt was obtained by boiling potassic molybdate with an excess of potassic hydrate, and adding a solution of PtCl₆H₂ until platinic hydrate which at first dissolves as fast as formed, was in small excess. Acetic acid was then added to an acid reaction. On standing fine granular yellow crystals were formed in quantity. These were dissolved in hot water and recrystallized. Of this salt :

0.5191 gram gave 0.0098 gram Pt = 2.20% PtO₂.

0.5191 gram gave 0.5665 gram MoS₃ = 81.85% MoO₃.

* Poggendoff, Annalen, CXXVII. 291.

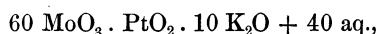
0.6459 gram lost on ignition with WO_4Na_2 0.0447 gram = 6.92%

$\text{O} + \text{H}_2\text{O} = 6.61 \text{ H}_2\text{O}$.

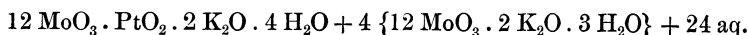
1.2241 grams lost on ignition with WO_4Na_2 0.0872 gram = 7.12%

$\text{O} + \text{H}_2\text{O} = 6.81 \text{ H}_2\text{O}$.

The analyses lead to the formula,



which may be written provisionally as

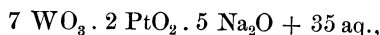


The formula requires :

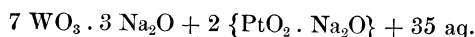
		Calculated.	Found.	
60 MoO_3	8640	82.04	81.85	
PtO_2	226.5	2.16	2.20	
10 K_2O	994	8.97	9.24	
40 H_2O	720	6.83	6.61	6.81
	<u>10530.5</u>	<u>100.00</u>		

This salt is readily soluble in hot water without apparent decomposition. It gives a very pale yellow crystalline precipitate with argentic nitrate and a pale greenish blue precipitate with cupric sulphate, which is soluble in an excess of this last.

Rosenheim has recently described* another platino-tungstate with the empirical formula,



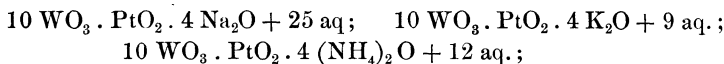
and regards it as a double salt,



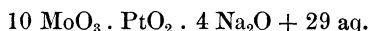
This salt was obtained by boiling normal sodic tungstate, WO_4Na_2 , in concentrated solution with platinic hydrate, and presented small yellow needles which could not be recrystallized without decomposition. He did not succeed in obtaining platino-tungstates by boiling platinic hydrate with various meta-tungstates, and suggests that the three salts which I described in my preliminary notice were mixtures of meta-tungstates (para-tungstates) and platinic oxide. They were, on the contrary, perfectly well defined and crystallized, as were also the platino-tungstates and platino-molybdates described in this paper. Further investigation will probably show that a number of other salts can be obtained by the method which I have described in which the

* Berichte der deutschen chem. Gesellschaft, XXIV. 2397.

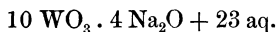
platinic hydrate is brought in contact with acid tungstates or molybdates in the nascent state. Phospho-platino-tungstates and similar molybdenum compounds appear also to exist. A solution of 24 : 1 : 2 phospho-tungstate of sodium readily dissolves platinic hydrate on boiling, and gives an orange-colored solution which after filtration and evaporation deposits ill defined orange crystals. When a solution of ammoniac chloride is mixed with the solution obtained as above, a beautiful orange crystalline salt is thrown down. In a preliminary notice published in 1877,* I have described the preparation and properties of platino-tungstates having respectively the formulas



and of a platino-molybdate with the formula



All of these tungstate compounds were obtained by boiling



with the soluble form of platinic hydrate. The molybdenum compound was obtained in a similar manner, but I am not now able to state what acid molybdate of sodium was employed. I have not succeeded in obtaining these compounds a second time, and in the long interval of time which has elapsed since the publication of my preliminary notice the notes of description and analyses have been lost. I can only express my conviction that more extended investigations will show that no error has been made, and that the compounds unite as described. I will further remark, that, taking the analyses which I have given in this paper, it may be possible to give simpler formulas for some at least of the salts described. The formulas given represent I believe most accurately the results of the analyses, but as the percentages of platinum are relatively small the quotients of these percentages by the atomic mass of platinum are very small divisors. On the other hand, the quotients obtained by dividing the percentages of tungstic or molybdic oxide by the molecular masses of tungstic or molybdic oxide are relatively very large, and the ratio between the two quotients in question becomes somewhat uncertain. The compounds which I have obtained by the method which I have given of bringing platinic oxide *in statu nascenti* into contact with the solutions

* Berichte der deutschen chem. Gesellschaft, X. 1384. Am. Journ. of Science, [3.], XIV. 61.

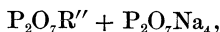
of acid tungstates or molybdates gives such well defined and beautifully crystalline salts that the subject will doubtless attract the attention of other chemists. I will make the suggestion that possibly the salts which I described in my preliminary notice may be obtained by adding ammoniac chloride to solutions of the double salts described in this paper, so as, in the case of the tungstic compounds at least, to precipitate the tungstic oxide not combined with platinic oxide in the form of



or an analogous salt. The solution should then contain only a platino-tungstate. The application to the platino-molybdates described is less probable.

SECOND SERIES OF PYROPHOSPHO-TUNGSTATES AND PYROPHOSPHO-MOLYBDATES.

When sodic pyrophosphate is added in excess to a solution containing a metallic salt, the precipitate which is at first found is in many cases redissolved with formation of a double salt of sodium and the metal in question. In a certain number of cases, the heavier metal in the new compound is not replaceable under ordinary conditions, and does not exhibit its characteristic reactions with tests. These facts are of course familiar to all chemists. Persoz supposed that these salts might be represented, in the case of divalent metals, by the general formula, as we should now write it,



and that the group $\text{P}_2\text{O}_7\text{R}''$ was to be regarded as electro-negative to the group $\text{P}_2\text{O}_7\text{Na}_4$, so that the compound would be simply analogous to ClNa . If we write the double salt $\text{P}_2\text{O}_7\text{R}''\text{Na}_2$, we may regard the complex $\text{P}_2\text{O}_7\text{R}''$ as playing the part of a relatively electro-negative group, as in the case of double cyanides, so called. Whether this view is to be considered as identical with that of Persoz, is a question about which opinions may differ, and which is not important for my present purpose. Admitting that the groups $\text{P}_2\text{O}_7\text{R}''$ or $\text{P}_2\text{O}_7\text{R}'''$ are transferable as such in their relatively simple alkaline salts, we may inquire whether they enter into the composition of complex acids, and if so, whether the compounds so formed differ from ordinary pyrophospho-tungstates and pyrophospho-molybdates. As the initial point in this investigation I have selected mangano-disodic pyrophosphate, $\text{P}_2\text{O}_7\text{Mn}_2\text{Na}_2$.

Mangano-sodic Pyrophospho-Molybdate.

In another part of this memoir I have described several salts belonging to the group of pyrophospho-tungstates. As these were peculiar in their constitution, it became a matter of interest to determine whether the pyrophospho-molybdates had a similar constitution, or, in other words, whether they contained the pyrophosphoric group $22 \text{RO}_3 \cdot 9 \text{P}_2\text{O}_7$ found in the salts of the tungstic series.

Molybdic teroxide boiled with sodic pyrophosphate, care being taken to keep the oxide in excess, is dissolved with much facility and in large quantity. The colorless solution may be evaporated to a syrup without yielding crystals on standing, and gives no precipitates with salts of potassium or ammonium. The solution, however, gives precipitates with salts of most of the heavier metals. Of these I selected the manganous compounds for special study, supposing that all the manganese would be present as base, and that a comparison could be made between salts of this type and those in which manganese exists in the pyrophosphoric molecule, and which I shall describe further on.

When a solution of manganous chloride is mixed with one of sodic pyrophospho-molybdate prepared as above, a dull buff-colored apparently amorphous precipitate is formed. On standing with an excess of the sodium salt, this was gradually converted into a mass of beautiful bright yellow crystals. These were well washed with cold water, and then dissolved in boiling water. The filtered solution gave on cooling a mass of sulphur-yellow crystals, which were again dissolved and recrystallized. The salt was then dried on woollen paper. It was analyzed by Mr. G. W. Patterson.

- { 1.3289 grams gave 0.1065 gram $\text{P}_2\text{O}_7\text{Mg}_2 = 5.13\% \text{P}_2\text{O}_5$.
- { 1.3289 grams gave 0.2486 gram $\text{P}_2\text{O}_7\text{Mn}_2 = 9.36\% \text{MnO}$.
- { 0.9538 gram gave 0.1819 gram $\text{P}_2\text{O}_7\text{Mn}_2 = 9.53\% \text{MnO}$.
- { 0.9538 gram gave 0.5934 gram $\text{P}_2\text{O}_5 + \text{MoO}_3 = 62.22\%$.
- 1.0960 grams lost with Wo_4Na_2 0.2037 gram = 18.56%.
- 0.9445 gram lost with Wo_4Na_2 0.1743 gram = 18.45%.

The analyses lead to the formula



which requires :

		Calculated.		Found.
22 MoO_3	3168	57.26	} 62.39	57.16
2 P_2O_5	284	5.13		5.13
7 MnO	497	8.99	} 19.07	9.36
9 Na_2O	558	10.08		9.84
57 H_2O	1026	18.54		18.58
	5533	100.00		18.45

The salt is nearly insoluble in cold water. Boiling water dissolves it, but the salt is decomposed, giving a pale yellow flocky precipitate and a sherry-wine colored solution. On standing a short time, the solution as it cools becomes pale yellow, and finally almost colorless, while the precipitate gradually becomes brighter yellow and crystalline, and the original salt appears to be again formed by recombination. Both the precipitate formed in the decomposition by boiling water and the wine-yellow solution give reactions with argentic nitrate which differ from one another as well as from the yellow crystalline silver salt formed by digesting the pyrophospho-molybdate of manganese and sodium with argentic nitrate.

In the analysis the solution of the salt was boiled with mercurous nitrate and mercuric oxide. The precipitate contained only molybdic and phosphoric oxides, and was free from manganese. There is therefore reason for assuming, as I have done, that all the manganese is basic, and that none is present in the form of the molecule P_2O_7Mn .

Mangano-ammonic Pyrophospho-Molybdates.

When manganeous pyrophosphate is digested for some time with a strong solution of 14:6 acid ammoniac molybdate, a buff-yellow very slightly soluble compound is formed. This is to be well washed, dried on woollen paper, and afterward *in pleno* over sulphuric acid. Of this salt, analyzed by Mr. G. W. Patterson:

0.7830 gram lost on ignition with WO_4Na_2 0.0778 gram $NH_3 + H_2O$
= 9.94%.

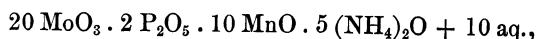
0.6554 gram lost on ignition with WO_4Na_2 0.0645 gram $NH_3 + H_2O$
= 9.84%.

0.8590 gram gave 0.0338 gram NH_3 = 3.92%.

0.7191 gram gave 0.0285 gram NH_3 = 3.97%.

{ 0.8725 gram gave 0.0881 gram $P_2O_7Mg_2$ = 6.46% P_2O_5 .
{ 0.8725 gram gave 0.2841 gram $P_2O_7Mn_2$ = 12.62% MnO .

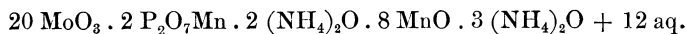
The analyses lead to the formula,



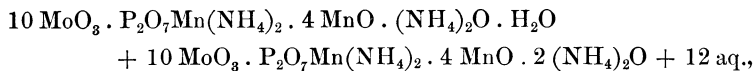
which requires:

		Calculated.		Found.	
20 MoO ₃	2880	66.76	} 73.34	67.27	} 73.73
2 P ₂ O ₅	284	6.58		6.46	
10 MnO	710	16.46		16.30	
10 NH ₃	170	3.94		3.92	3.97
15 H ₂ O	270	6.26		5.94	
	<u>4314</u>	<u>100.00</u>			

In the analyses the salt was digested for some time at a boiling heat with mercurous nitrate and mercuric oxide. The mercurous salt formed contained manganous oxide. The precipitate was fused with a mixture of potassic and sodic carbonates to separate manganous oxide. The filtrate from this last gave the phosphoric pentoxide. Molybdic teroxide was determined by difference. As the salt could not be recrystallized, the defects in the analysis are doubtless chiefly due to traces of impurity. The formula of the salt should be written, according to my view :



We may have here a double salt, as, for instance,



but of course other arrangements are possible.

The manganese in the molecule containing P₂O₇ may be called, for convenience, the internal or fixed manganese, to distinguish it from the external or basic manganese. To determine if possible the ratio between the external and internal manganese, I digested a weighed portion of the salt in the cold for twelve hours with mercurous nitrate, and then boiled, adding a little mercuric oxide in the usual manner. In the filtrate, after separating the mercury, the manganese was determined as P₂O₇Mn₂. In this manner,

1.2306 grams gave 0.3520 gram P₂O₇Mn = 11.08 %.

From this it appears that about $\frac{1}{12}$ of the manganese was precipitated by mercurous nitrate, in place of $\frac{1}{10}$. If, therefore, we consider $\frac{1}{10}$ of the manganese to be present in the salt as P₂O₇Mn, we must suppose that this molecule is broken up, to a certain extent at least, by boiling with mercurous nitrate, and it is very doubtful whether the manganous oxide exists in any other form than as a base. Certainly

there is no sufficient evidence that it forms here an integrant molecule P_2O_7Mn , as in sodio-manganous pyrophosphate, $P_2O_7Mn \cdot Na_2$. I regard the question, however, as still an open one, since the molecule P_2O_7Mn , assuming its existence, may be decomposed by mercurous nitrate and give a corresponding mercurous integrant molecule $P_2O_7Hg_2$, and since the salt is decomposed by water like the other salts of this series. It appears also from the above that the pyrophospho-molybdates do not correspond in composition to the pyrophospho-tungstates. At least I have not found in them the molybdenum molecule corresponding to the tungstic molecule, $22 WO_3 \cdot 9 P_2O_7$. It must, however, be remarked that, as I shall show, the pyrophospho-tungstates which contain manganese do not contain this molecule.

Mangano-sodic Pyrophospho-Tungstates.

These salts are very easily formed by boiling manganous pyrophosphate with acid tungstates. Dark sherry-wine colored solutions are formed, which in cooling deposit crystals in abundance.

14 : 1 : 3 : 6 *Mangano-sodic Pyrophospho-Tungstate.* This salt is formed more conveniently by mixing a solution of 12 : 5 sodic tungstate with manganous pyrophosphate and digesting for some hours in a closed bottle heated in a water bath. The pyrophosphate must be in excess. It dissolves rather slowly to a fine deep orange-colored liquid, which after evaporation deposits beautiful crystals, which may be redissolved and recrystallized. In spite of the employment of an excess of manganous pyrophosphate, it is rather difficult to obtain a solution of the salt which is perfectly saturated with the manganous salt. The crystals have a brownish orange color. They effloresce in dry air, though not rapidly, but *in pleno* over sulphuric acid they lose water in relatively large quantity. Of this salt, analyzed by Mr. G. W. Patterson:

1.4176 grams lost on ignition with WO_4Na_2 0.2032 gram = 14.34% water.
 1.2375 grams gave 0.0611 gram $P_2O_7Mg_2$ = 3.16% P_2O_5 .
 { 1.0476 grams gave 0.1041 gram $P_2O_7Mn_2$ = 4.97% MnO .
 { 1.0476 grams gave 0.7650 gram $WO_3 + P_2O_5$ = 73.05%.

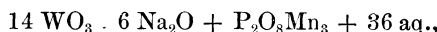
The analyses lead to the formula,



which requires:

		Calculated.		Found.	
14 WO ₃	3248	70.25	} 73.32	69.89	} 73.05
P ₂ O ₅	142	3.07		3.16	
3 MnO	213	4.62	} 12.66	4.97	} 12.65
6 Na ₂ O	372	8.04		7.68	
36 H ₂ O	648	14.02		14.34	
	<u>4623</u>	<u>100.00</u>			

We may give this salt the formula

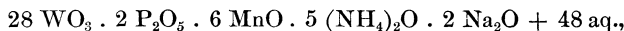


if we suppose that the pyrophosphate of manganese has become orthophosphate. Both constituents are then normal salts.

The ammonium salt was prepared by double decomposition between the sodium salt and ammoniac chloride, and repeated crystallization. It presented orange-colored prismatic crystals, very soluble in both hot and cold water. Of this salt :

0.7846 gram gave 0.01715 gram NH₃ = 2.19%.
 0.6556 gram gave 0.01394 gram NH₃ = 2.13%.
 0.4886 gram gave 0.0594 gram NH₃ + H₂O = 12.16%.
 1.0895 grams gave 0.1162 gram P₂O₇Mn₂ = 5.83% MnO.

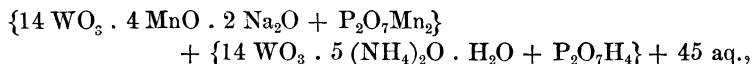
The analyses correspond well with the formula,



which requires :

		Calculated.	Mean.		
28 WO ₃	6496	77.67	77.76	77.84	77.69
2 P ₂ O ₅	284	3.40	3.13	3.13	
6 MnO	426	5.09	5.39	5.33	5.45
10 NH ₃	170	2.03	2.16	2.13	2.19
2 Na ₂ O	124	1.48	1.56	1.56	(diff.)
48 H ₂ O	864	10.33	10.00	10.00	
	<u>8364</u>	<u>100.00</u>			

We may formulate this salt as



the type being $14 \text{ WO}_3 \cdot 6 \text{ RO} + \text{P}_2\text{O}_7\text{R}'_4$, so that so far as the empirical constitution is concerned the salt may be regarded as a double salt of two normal constituents. The analyses were made by Mr. G. W. Patterson.

Auramin Pyrophosphates.

When a solution of double chloride of gold and sodium AuCl_4Na is made as nearly neutral as possible and then boiled with sodic pyrophosphate $\text{P}_2\text{O}_7\text{Na}_4$, a very pale yellow solution is formed, which contains the auro-sodic salt discovered by Persoz, the formula of which we should now write $\text{P}_2\text{O}_7\text{Au}'''\text{Na}$. The solution of this salt gives with ammonia a white precipitate which quickly becomes yellow and crystalline. With argentic nitrate it gives a pale yellow flocky crystalline precipitate, which is very insoluble and does not blacken readily in the light. With mercurous nitrate it gives a greenish gray flocky crystalline precipitate. A nearly white curdy precipitate is formed with sulphate of luteo-cobalt; none with sulphate of croceo-cobalt. With $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ gold is reduced.

The crystalline precipitate formed by ammonia in the auro-sodic pyrophosphate solution was well washed, dried at 150° , and analyzed.

0.9665 gram gave 0.6756 gram gold = 78.44% Au_2O_3 .

0.9031 gram gave 0.7003 gram gold = 78.34% Au_2O_3 .

0.9665 gram gave 0.1621 gram $\text{P}_2\text{O}_7\text{Mg}_2$ = 10.73% P_2O_5 .

1.0031 grams gave 0.1703 gram $\text{P}_2\text{O}_7\text{Mg}_2$ = 10.86% P_2O_5 .

0.7375 gram gave 0.02286 gram NH_3 = 3.10%.

0.7691 gram lost, at 150°C ., 0.0420 gram water = 5.46%.

The analyses lead to the formula



which requires:

		Calculated.	Found.	
14 Au_2O_3	6178	78.34	78.44	78.34
6 P_2O_5	852	10.80	10.73	10.86
14 NH_3	238	3.02		3.10
3 Na_2O	186	2.36		2.26 (diff.)
24 H_2O	432	5.48		5.46
	7886	100.00		

The analysis is due to Dr. Morris Loeb, who assisted me in this part of my work most efficiently.

The salt does not explode at low temperatures, but on heating to a little above 170°C . a violent explosion takes place. This shows clearly that part at least of the gold is in the form of an auramin, or compound with ammonia.

The auramin pyrophosphate of sodium, on boiling with baric chloride, gives a yellow crystalline salt; with mercuric chloride, a fine pale yellow crystalline salt which becomes very distinct on boiling.

When the auramin salt is boiled with mercurous nitrate, some mercury is reduced to metal, and at the same time very characteristic white prismatic crystals are formed. Chlorhydric acid does not sensibly dissolve the pyrophosphate, but changes it to a pale yellow flocky crystalline body. Chloride of luteo-cobalt gives on boiling an orange crystalline salt.

When the crystalline yellow or dull orange baric salt is well washed with hot water and then filtered off, the colorless filtrate on evaporation gives with sodic hydrate a very distinct reaction for ammonia. Part of the ammonia in the salt must therefore have been in the form of ammonia, unless we admit that the auramin is decomposed under the circumstances. When treated with a cold solution of argentic nitrate reaction sets in at once, and a fine yellow flocky crystalline salt is formed; but no trace of ammonia is obtained from the filtrate after washing the salt with cold water and separating the excess of silver. Both the barium and silver salts were partially analyzed.

The barium salt was analyzed by Mr. G. W. Patterson :

0.6472 gram	gave 0.1015 gram BaSO_4	= 10.30% BaO .
0.6472 gram	gave 0.1426 gram $\text{P}_2\text{O}_7\text{Mg}_2$	= 14.09% P_2O_5 .
0.6472 gram	gave 0.3900 gram gold	= 67.63%.

Here the ratios are $9 \text{ Au}_2\text{O}_3 : 6 \text{ P}_2\text{O}_5 : 4 \text{ BaO}$.

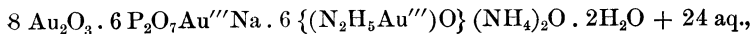
In the silver salt (Patterson) :

0.7718 gram	0.0915 gram AgCl	= 9.58% Ag_2O .
0.7718 gram	0.4470 gram gold	= 64.98%.
0.7718 gram	0.1584 gram $\text{P}_2\text{O}_7\text{Mg}_2$	= 13.13% P_2O_5 .

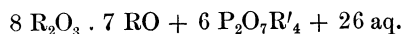
The ratios are approximately $16 \text{ Au}_2\text{O}_3 : 10 \text{ P}_2\text{O}_5 : 5 \text{ Ag}_2\text{O}$.

The analyses of the barium and silver salts are at least sufficient to show that no simple double decomposition takes place in either case. The formula which I have given for the gold salt is to be regarded as purely empirical, and does not explain the explosive character of the salt. No compounds falling under the general expression $\text{Au}_2(\text{NH}_3)_n\text{O}_3$ are at present known. Dumas and Raschig give to fulminating gold the formula $\text{NH}_2 \cdot \text{Au}''' \cdot \text{NH}$, which may be written $\text{N}_2\text{H}_3\text{Au}'''$. This is equivalent to 2 NH_3 ; the corresponding ammonium must be $\text{N}_2\text{H}_3\text{Au}''' \text{H}_2$, and the oxide of this $(\text{N}_2\text{H}_5\text{Au}''')\text{O}$. If

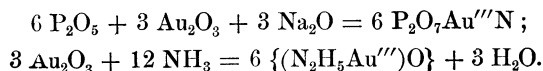
we assume that this oxide is present in the auramin pyrophosphate which I have described, we may write the formula



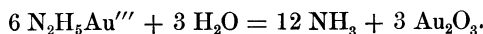
which is reducible to the type



As regards the deduction of the formula from the analyses, it may be worth while to give also the equations



In the determination of the ammonia by boiling with KHO or NaHO, we have

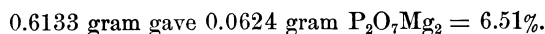


Auro-pyrophospho-Molybdates.

When a solution of chloro-aurate of sodium, AuCl_4Na , is mixed with one of pyrophospho-molybdate of sodium, a dull orange-colored fine-grained crystalline precipitate is thrown down, which is almost certainly an auro-pyrophospho-molybdate of sodium. When a solution of auro-pyrophosphate of sodium, $\text{P}_2\text{O}_7\text{AuNa}$, is boiled for some time with 14:6 molybdate of ammonium, a pale buff-colored crystalline precipitate is formed, which is slightly soluble in boiling water, giving however only a turbid liquid. After washing with cold water this precipitate was dried *in pleno* over sulphuric acid. Of this salt:

- 0.5581 gram lost by ignition with WO_4Na_2 0.0841 gram = 15.07% $\text{H}_2\text{O} + \text{NH}_3 + \text{O}$.
- { 0.8123 gram gave 0.3489 gram gold = 42.94% = 48.18% Au_2O_3 .
- { 0.8123 gram gave 0.0837 gram $\text{P}_2\text{O}_7\text{Mg}_2$ = 6.59% P_2O_5 .
- 0.6133 gram gave 0.2615 gram gold = 42.13% = 47.85%.
- 0.2746 gram gave 0.01558 gram NH_3 = 5.65% NH_3 .
- 0.4774 gram lost by ignition with WO_4Na_2 0.0744 gram = 15.58%.

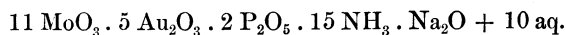
In this last analysis the salt had probably absorbed a little water. The same is true for the next:



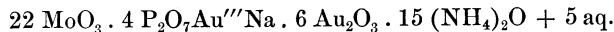
If we calculate the analyses for an anhydrous salt, we find:

		Calculated.	Found.	
11 MoO ₃	1584	36.07		
5 Au ₂ O ₃	2206	50.25	50.29	50.27
2 P ₂ O ₅	284	6.46	6.87	6.83
15 NH ₃	255	5.81	5.89	
Na ₂ O	62	1.41		
	4391	100.00		

In the hydrated salt the ratios are nearly



The formula requires 3.93% of water. The mean of the water in the two analyses is 4.18. It is to be borne in mind that the salt could not be recrystallized, and was probably not absolutely pure. The salt does not explode on heating, but merely "puffs." Hot dilute chlorhydric acid readily dissolves it. Ammonia water does not sensibly dissolve it, but gives an orange-colored substance which may be the corresponding auramin compound. The formula may be written provisionally



More extended investigations are necessary to fix the formulas of this and analogous compounds. Analysis by Mr. G. W. Patterson.

Auramin-pyrophospho-Molybdates.

When the orange-colored flocky precipitate formed by adding ammonia to auro-pyrophosphate of sodium is boiled for some time with 14:6 ammonic molybdate, and the whole allowed to stand with the supernatant liquid, a pale yellowish crystalline salt is formed. After thorough washing with cold water, the salt was dried on bibulous paper and *in pleno* over sulphuric acid. For analysis it was boiled for a short time with a mixture of chlorhydric and sulphurous acids. The phosphoric acid was determined in the filtrate from the gold by magnesia mixture, in the manner which I have pointed out in treating of the analysis of the phospho-molybdates.* The filtrate from the ammonio-magnesian phosphate, after adding (NH₄)₂S, was evaporated, filtered to separate free sulphur, and then treated with cold dilute chlorhydric acid. The precipitated MoS₃ was filtered on a Gooch filter, washed, dried at 106° C., then washed several times with carbon disulphide, dried, and weighed. Ammonia was determined by boiling with sodic hydrate and titration.

* Proceedings of the American Academy, XXIX. 64.

- (1) 0.3969 gram gave 0.0217 gram $\text{NH}_3 = 5.47\%$.
- (2) 0.5733 gram gave 0.3612 gram gold = 70.68%.
- (3) 0.5733 gram gave 0.1168 gram $\text{P}_2\text{O}_7\text{Mg}_2 = 13.03\% \text{P}_2\text{O}_5$.
- (4) 0.5733 gram gave 0.0426 gram $\text{MoS}_3 = 5.57\% \text{MoO}_3$.
- (5) 0.3499 gram lost on ignition with WO_4Na_2 0.0703 gram = 20.09%.

The salt explodes on heating, but not violently. There appears to have been a slight loss on heating with sodic tungstate, and I have accordingly calculated the water by difference, all the other constituents having been determined directly. The analyses correspond to the formula $12 \text{Au}_2\text{O}_3 \cdot 3 \text{MoO}_3 \cdot 7 \text{P}_2\text{O}_5 \cdot 24 \text{NH}_3 + 21 \text{aq}$. Analysis by Mr. G. W. Patterson :

		Calculated.	Found.
12 Au_2O_3	5297	70.54	70.68
3 MoO_3	432	5.75	5.57
7 P_2O_5	994	13.23	13.03
24 NH_3	408	5.44	5.47
21 H_2O	378	5.04	5.25
	<u>7509</u>	<u>100.00</u>	

Here, as in the cases of the other gold compounds, part of the ammonia is present as ammoniac oxide and part is directly combined with gold; but the proportions remain to be determined. The careful study of this class of compounds appears likely to lead to very interesting results. I have classed them only provisionally with complex acids.

As it may not be possible for me to return to the subject,* I will here give the results of some preliminary work, which will at least serve as starting points for further investigation.

Molybdico-Tungstates.

When acid molybdate of ammonium is boiled with chlorhydric acid and potassic iodide, and the deep orange-colored liquid is precipitated with ammonia, a brown precipitate of $\text{Mo}(\text{OH})_4$ is thrown down, which after thorough washing is readily soluble in a solution of 12 : 5 sodic tungstate, forming a deep orange-red liquid. Potassic bromide gives a buff-colored crystalline precipitate, which is soluble in boiling water, and crystallizes on cooling in small pale brown scales. Ammoniac chloride gives a similar salt, as do also the chlorides of barium, strontium, and calcium. All these salts are soluble in hot water, and separate from the solution in pale brown crystals. In

* "A rebus gerendis senectus abstrahit." — Cicero, *Cato Major*.

preparing the potassium salt a large excess of potassic bromide should be used: the bromide in this, as in many other cases, appears to be preferable to the chloride and nitrate. In these salts the molybdic dioxide may be easily and accurately determined by titration with permanganate, after adding sulphuric acid. The solutions of the molybdico-tungstates readily absorb oxygen from the air, forming molybdic teroxide, a fact which must be taken into account in analysis.

Molybdic hydrate, $\text{Mo}(\text{OH})_4$, quickly reduces MoO_3 in a solution of 14 : 6 ammonium salt, and gives a fine blue liquid, which probably contains Mo_2O_5 or $\text{MoO}_2 + \text{MoO}_3$. When a very cold solution of ammonic molybdate is employed, and molybdic hydrate is added in small portions at a time, the solution becomes yellow, then quickly green, and finally blue. It is possible that a molybdico-molybdate, $m\text{MoO}_2 \cdot n\text{MoO}_3 \cdot p\text{R}_2\text{O}$, is formed at first. Molybdic hydrate reduces both molybdic and tungstic teroxides in phospho-molybdates and phospho-tungstates. Analyses of the potassium, calcium, and barium molybdico-tungstates were made with salts which perhaps were not absolutely pure. The formulas obtained appeared to be respectively $12 \text{WO}_3 \cdot \text{MoO}_2 \cdot 5 \text{K}_2\text{O} + 16 \text{aq.}$; $12 \text{WO}_3 \cdot \text{MoO}_2 \cdot 5 \text{CaO} + 32 \text{aq.}$; and $12 \text{WO}_3 \cdot \text{MoO}_2 \cdot 6 \text{BaO} + 30 \text{aq.}$; but these are given with much reserve. In these the molybdenum was determined by titration with permanganate, and the sum of the molybdic and tungstic teroxides, after oxidation, by precipitation of the neutral solution with calcic or baric chloride. Tungstic teroxide could then be determined by difference.

It seems at least probable that tungstico-molybdates corresponding to molybdico-tungstates, as, for example, $12 \text{MoO}_3 \cdot \text{WO}_2 \cdot x \text{RO}$, also exist.

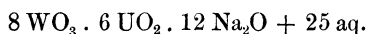
Uranoso-Tungstates.

When uranic oxide is dissolved in dilute sulphuric acid, and the solution is treated with metallic zinc, a solution of sulphate of uranic dioxide is formed which after a time deposits a gray-green powder insoluble in cold water, and probably a basic sulphate. This body treated with a solution of 12 : 5 sodic tungstate gives at once an olive-green crystalline salt very insoluble in hot water. The supernatant liquid has a peculiar reddish tint. The dark olive-green salt is oxidized by boiling with nitric acid and gives a yellowish white mixture, or possibly compound, of uranic and tungstic teroxides, easily decomposed by boiling with caustic alkalies, with separation of uranic oxide and formation of sodic tungstate. A solution of 12 : 5 potassic

tungstate acts in the same manner upon the uranious salt, giving also an olive-green crystalline salt and a brown-red solution. Similar results were obtained with acid ammonic tungstate. After drying for some days upon paper, the sodium salt was analyzed by Dr. Loeb:

0.4436 gram lost with WO_4NO_2 0.0331 gram = 7.46%.
 { 0.9861 gram gave 0.3954 gram WO_3 = 40.09%.
 { 0.9861 gram gave 0.3360 gram UO_2 and KMnO_4 = 34.08%.

The analyses lead to this formula,



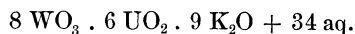
		Calculated.		Found.
8 WO_3	1856	39.69	} 74.46	40.09
6 UO_2	1626	34.77		34.08
12 Na_2O	744	15.92		16.46 (diff.)
25 H_2O	450	9.62		9.47
	4676	100.00		

The water determination was made by heating with sodic tungstate and determining the loss of weight. In the fusion the UO_2 is completely reoxidized to UO_3 . Hence a correction must be applied to the water, which in the above case amounts to 2.01% to be added. As the salt could not be recrystallized, it was doubtless not perfectly pure.

The olive-green potassium salt is also insoluble in hot water and in chlorhydric acid. It reduces silver and mercury from their nitrates, and appears to undergo double decomposition with baric and calcic chlorides. This salt was also analyzed by Dr. Loeb:

{ 1.3260 grams gave 0.4997 gram WO_3 = 37.69%.
 { 1.3260 grams gave with KMnO_4 gram UO_2 = 33.21%.
 0.9275 gram lost on ignition with WO_4Na_2 0.0833 gram = 8.98%.

The analyses lead to the formula,



		Calculated.		Found.
8 WO_3	1856	37.58	} 70.50	37.69
6 UO_2	1626	32.92		33.21
9 K_2O	846	17.12		16.60 (diff.)
34 H_2O	612	12.38		12.50
	4940	100.00		

The potassic salt corresponds in constitution to the sodic salt if we write it:



Silico-Molybdates.

The existence of definite silico-molybdates appears to have been first observed by Parmentier,* who obtained potassium, sodium, and ammonium salts by the action of alkaline silicates upon alkaline molybdates in presence of nitric acid. The free acid has the formula $12 \text{ MoO}_3 \cdot \text{SiO}_2 + 26 \text{ aq.}$ I have devised another method of preparing this class of salts, which may perhaps be generalized in its application. When a solution of fluosilicic acid is poured into one of 14 : 6 molybdate of ammonium, no precipitate is formed, but the solution becomes yellow. On evaporation a bright yellow crystalline body separates in large quantity. When normal sodic molybdate, MoO_4Na_2 , is strongly acidulated with chlorhydric acid, the addition of fluosilicic acid gives at once a bright yellow color. The solution obtained in this manner gives no precipitate in the cold with ammonic chloride, but on boiling and shaking for a few minutes a beautiful bright yellow crystalline precipitate is thrown down in abundance. This is slightly soluble in hot water to a yellow liquid. A solution of fluosilicic acid mixed with one of an acid potassic molybdate forms no precipitate, but the mixture is yellow, and on evaporation to dryness upon a water bath yields a highly crystalline yellow powder. Much molybdic teroxide is at the same time reduced to blue oxide. The yellow solutions of the silico-molybdates of potassium and sodium give with nitrate of croceocobalt a beautiful orange crystalline precipitate, which is insoluble in cold water and readily washed and dried. The bright yellow silico-molybdate of ammonium after careful washing was analyzed :

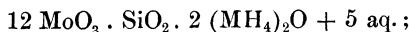
0.7963 gram lost on ignition with WO_4Na_2 0.0750 gram NH_3 and $\text{H}_2\text{O} = 9.42\%$.

0.5279 gram left on ignition 0.0158 gram $\text{S} : \text{O}_2 = 2.99\%$.

0.6504 gram gave 0.0339 gram $(\text{NH}_4)_2\text{O} = 5.22\%$.

0.5817 gram gave 0.03045 gram $(\text{NH}_4)_2\text{O} = 5.23\%$.

The analyses correspond to the formula,



which requires :

		Calculated.	Found.	
12 MoO_3	1728	87.18	87.58 (diff.)	
SiO_2	60	3.03	3.00	
2 $(\text{NH}_4)_2\text{O}$	104	5.24	5.22	5.23
5 H_2O	90	4.55	4.20	
	1982	100.00		

* Comptes Rendus, XCII. 1234, and XCIV. 213.

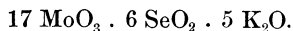
The silica was determined by igniting the salt with free access of air until all the molybdic oxide was expelled. The reactions of a solution of the sodium salt were as follows. No precipitate with baric and calcic chlorides. None at first with potassic bromide, but on standing bright yellow crystals formed. A sulphur yellow crystalline precipitate with mercuric nitrate and a beautiful bright orange-yellow highly crystalline precipitate with mercurous nitrate. A very pale yellow crystalline precipitate with argentic nitrate and a pale yellow fine-grained crystalline precipitate with thallous nitrate. Pechard * has obtained the same salt by precisely the same process as that which I have employed, and has priority in publication. I have also obtained a titanio-molybdate and a zirconio-molybdate by similar methods, but have not analyzed them. Pechard has described beautiful salts of the two series, and rendered further work on my part unnecessary.

Selenoso-Molybdates.

When 24 : 1 phospho-molybdate of potassium is boiled with a solution of potassic selenite SO_3K_2 it readily dissolves to a perfectly clear and colorless liquid, which after an hour deposits beautiful large granular colorless crystals in abundance. These are readily soluble in hot water, and crystallize from the solution without change, except that large transparent colorless crusts are obtained. Of this salt, analyzed by Mr. G. W. Patterson :

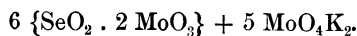
{ 1.1360 grams gave 0.1503 gram of selenium = 13.23% = 18.09% SeO_2 .
 { 1.1360 grams gave 0.7772 gram PtCl_6K_2 = 13.27% K_2O .
 0.9570 gram lost up to 175° C. 0.0058 gram H_2O = 0.61%.

Deducting the small percentage of water, the analyses correspond to the formula.



		Calculated.	Found.
17 MoO_3	2448	68.81	68.45
6 SeO_2	648	18.16	18.20
5 K_2O	472	13.23	13.35
	<u>3568</u>	<u>100.00</u>	

The formula may also be written,



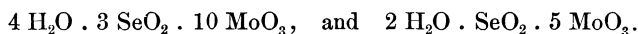
* Comptes Rendus, CXVII. 691-694. Cited in Zeitschrift für anorg. Chemie, VI. 200.

The selenium was determined by reduction with sulphurous acid and the molybdic oxide by difference. In spite of the mode of preparation, the salt did not contain phosphoric pentoxide. On repeating the preparation of the salt I obtained different results, the proportions used being probably not the same. The solution deposited first groups of colorless crystals, and then gave after further evaporation a white granular crystalline salt. The grouped crystals seemed at first to be quite insoluble in water, but when boiled dissolved, and then crystallized out very readily. Perhaps more than one salt was formed in this operation. The solution of the salt analyzed gave pale yellow crystalline precipitate with argentic and mercurous nitrates.

Selenoso-Tungstates.

When ammoniac tungstate is boiled with a solution of SeO_3H_2 it readily dissolves to a pale yellow solution, which almost immediately gives beautiful shimmering scales in a pale yellow mother liquor. These pass at once through a filter and are difficult to separate and wash. Potassic tungstate also readily dissolves in a solution of selenious acid, forming a pale yellow solution which on heating suddenly becomes opaque, while a pale yellow precipitate is thrown down. When washed by decantation with cold water, both the ammoniac and potassic salts have a distinct pale yellow color. When a solution of selenious acid is mixed with one of 12 : 5 sodic tungstate and a solution of potassic bromide is added, a white precipitate in very minute granular crystals is formed, settling rather slowly, and very slightly soluble in hot water. A solution of argentic nitrate gave, with the well washed salt, large very pale yellow crystalline flakes. Mercurous nitrate gave a pale yellow crystalline precipitate. A solution of selenious acid mixed with one of 24 : 1 : 2 sodic phospho-tungstate gave a white granular precipitate very slightly soluble in hot water. After careful washing, this gave, on boiling with argentic nitrate, a perfectly white crystalline salt, a bright yellow crystalline precipitate with mercurous nitrate, and a white crystalline precipitate with baric chloride. It is possible that phospho-selenoso-tungstates are formed in this manner.

Pechard* has recently described salts of two series of molybdoselenites, as he terms them, having respectively formulas which would indicate that they are derivatives of the acids :



* Comptes Rendus, CXVI. 1441-1444; also, CXVII. 104-106.

The same chemist has also described a very interesting series of salts, which he terms molybdo-sulphites, embraced under the general formula,



Telluroso-Molybdates and Tungstates.

Klein * many years since also observed the existence of complex acids containing tellurous and telluric oxides and tungstic oxide. So far as I am aware, no analyses have been published. A preliminary notice of my own work was communicated to the Harvard Chemical Club, February 12, 1884.†

When a solution of TeBr_6K_2 is formed with a large excess of water, the salt is completely decomposed into bromhydric and tellurous acid TeO_3H_2 . A solution of 14 : 6 acid molybdate of ammonium readily dissolves this last on boiling, and the clear filtered solution soon deposits beautiful granular colorless crystals in quantity. It is best to use an excess of tellurous acid. The telluroso-molybdate is much less soluble than the acid molybdate of ammonium, and may be redissolved and recrystallized without apparent decomposition. When a solution of the TeBr_6K_2 is mixed with one of the acid molybdate, a very pale yellow precipitate is formed. After standing, small bright yellow crystals also appear. The white precipitate is probably only tellurous acid. When freshly precipitated tellurous acid is boiled with a strong solution of an acid potassic tungstate, it does not dissolve, but changes character and becomes more distinctly crystalline. A solution of TeBr_6K_2 gives with one of 24 : 1 : 2 phospho-tungstate of sodium a very white granular precipitate, which is insoluble, and may be washed with boiling, but then settles slowly. The tellurium employed was the best commercial product, and doubtless not absolutely pure. If, as has been supposed, two different metals are embraced under the name, it is possible that the compounds of the two oxides with molybdic and tungstic oxides may afford means of separation in consequence of differences in composition and properties. Should tellurium be hereafter found to possess a technical value or interest, an abundant supply can be furnished by the mines of Colorado. The very high cost of the metal at present has prevented further study on my part.

* Bull. de la Société Chimique, [2.], XLII. 169.

† See also Berichte der deutschen chem. Gesellschaft, XVIII. 1089. August, 1884.

Cerico-Molybdates.

When ceric fluoride, CeF_4 , is boiled in a platinum dish with 14 : 6 molybdate of ammonium, the solution quickly becomes yellow, and soon deposits a fine yellow crystalline salt, which may be washed with cold water, in which it is but slightly soluble. It contains molybdic teroxide, ceric oxide, and ammonia. Basic ceric nitrate treated with a solution of hydro-potassic fluoride, KF_2H , changes character at once and becomes flocky-crystalline. After washing with cold water, boiling with 14 : 6 molybdate of ammonium dissolves but little, but the salt becomes bright sulphur-yellow and crystalline and is practically insoluble in water. The best method of preparing this salt consists in first preparing pure basic nitrate of cerium* free from lanthanum and didymium (neo-dymium and praseo-dymium). This is to be dissolved in nitric acid and the solution diluted. Acid potassic fluoride then precipitates a nearly white flocky salt, which dissolves readily in a boiling solution of 14 : 6 molybdate of ammonium to a yellow solution, and crystallizes from this. It will probably be better to boil with a solution of an acid sodic molybdate, as this yields a soluble sodic salt, the solution of which gives with ammoniac chloride a yellow crystalline precipitate of an ammonium salt, which will make a good starting point for further investigations.

When the ceric fluorine salt, prepared as above with KF_2H , is boiled with 10 : 4 sodic tungstate, a fine bright yellow solution is formed which gives a beautiful orange crystalline precipitate with nitrate of croceo-cobalt. In preparing the fluorine compound it is best to add a cold filtered solution of KF_2H to the basic ceric nitrate diffused in cold water, and not to heat at all. Ceric hydrate dissolves with difficulty in solutions of acid tungstates and molybdates, more easily when precipitated from cold solutions.

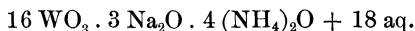
NOTE ON CERTAIN TUNGSTATES, AND ON A NEW
PHOSPHO-TUNGSTATE.

In other instalments of my work I have endeavored to show† that there exists a special class of metatungstates, of which the lowest term has the general formula $4\text{WO}_3 \cdot \text{RO}$, and the highest the general formula $24\text{WO}_3 \cdot 11\text{R}_2\text{O}$. This view appeared to be supported both by my own work and by that of Marignac, but has not found favor

* See my paper in American Journal of Science, XXXVII. 352.

† Proceedings of the American Academy, XV. 15.

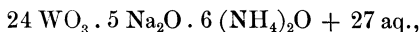
with chemists, and has in fact, so far as I am aware, passed wholly unnoticed. The highest term actually obtained by me* appeared to have the formula:



The only complete analysis made agreed well with this formula, and differed very materially from that of the 12:5 ammonia-sodic tungstate. As it has been asserted, however, that the two are identical, Mr. Charles D. Smith has made in my laboratory four analyses with portions of the salt which had been preserved. The analyses are as follows:

0.7226 gram	gave 0.6038 gram	= 83.55% WO_3 .
1.1598 grams	gave 0.9687 gram	= 83.54% WO_3 .
1.3281 grams	gave 1.1091 grams	= 83.51% WO_3 .
1.4740 grams	gave 1.2309 grams	= 83.50% WO_3 .
1.2726 grams	gave 0.0604 gram	$(\text{NH}_4)_2\text{O} = 4.75\%$.
1.0901 grams	gave 0.0508 gram	$(\text{NH}_4)_2\text{O} = 4.66\%$.
1.1360 grams	gave 0.0532 gram	$(\text{NH}_4)_2\text{O} = 4.67\%$.
0.6756 gram	gave 0.0318 gram	$(\text{NH}_4)_2\text{O} = 4.72\%$.
4.4687 grams	lost on ignition 0.5292 gram	= 11.84% NH_3 and H_2O .
3.0697 grams	lost on ignition 0.3638 gram	= 11.84% NH_3 and H_2O .
4.6030 grams	lost on ignition 0.5444 gram	= 11.82% NH_3 and H_2O .
3.3885 grams	lost on ignition 0.4014 gram	= 11.84% NH_3 and H_2O .

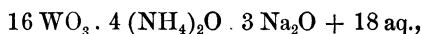
The analyses correspond to the formula,



which requires:

		Calculated.	Mean.	I.	II.	III.	IV.
24 WO_3	5568	83.40	83.52	83.55	83.54	83.51	83.50
6 $(\text{NH}_4)_2\text{O}$	310	4.68	4.70	4.75	4.66	4.67	4.72
5 Na_2O	312	4.65	4.65	—	—	—	—
27 H_2O	486	7.27	7.13	7.08	7.14	7.16	7.11
	6676	100.00					

The sodic oxide is determined by difference. The analyses agree rather more closely with the new formula than with that formerly given, which I will cite for the sake of comparison:



requires:

* Ibid., XVI. 76.

		Calculated.	Found.
16 WO ₃	3712	83.77	83.94
4 (NH ₄) ₂ O	208	4.69	4.64
3 Na ₂ O	186	4.20	4.21
18 H ₂ O	324	7.32	7.21
	4430	100.00	

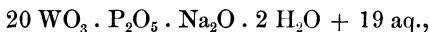
It is certainly difficult to decide between these two formulas, only it must be observed that the higher formula is derived from the mean of four analyses, which agree well with each other, and has therefore the weight of analytical evidence in its favor until further research shall prove its inaccuracy. Still another formula has been proposed by Von Knorre,* who writes $12 \text{ WO}_3 \cdot 3 (\text{NH}_4)_2 \cdot 2 \text{ Na}_2\text{O} + 13 \text{ aq.}$, which requires 84.41% WO₃, 4.73% (NH₄)₂O, 3.76% Na₂O, and 7.10% H₂O. The correspondence between the results of the analyses and the data required by the formula is much less than with the formula which I first gave and which Von Knorre rejects, and of course still less than with the new formula.

New Phospho-Tungstate.

Pure normal sodic tungstate was mixed in solution with sodic orthophosphate, PO₄Na₂H + 12 aq., in the proportion of twelve molecules of the first to one of the second salt, and chlorhydric acid added in small excess. A phospho-tungstate crystallized from the solution, and was redissolved and twice recrystallized. The new salt was in fine colorless crystals, less soluble than the now well known salt which has the formula, $24 \text{ WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 2 \text{ Na}_2\text{O} + 27 \text{ aq.}$ The salt was dried on paper for analysis. It effloresced or became opaque in dry air. Mr. Charles D. Howard obtained the following results on analysis.

1.4941 grams lost on ignition with WO₄Na₂ 0.1078 gram = 7.21% H₂O.
 1.4502 grams lost on ignition with WO₄Na₂ 0.1046 gram = 7.21% H₂O.
 1.0950 grams gave 1.0019 grams WO₃ + P₂O₅ = 91.49%.
 1.1950 grams gave 1.0975 grams WO₃ + P₂O₅ = 91.58%.
 1.6782 grams gave 0.0720 gram WO₃ + P₂O₅ = 2.74% P₂O₅.

The analyses lead to the formula,

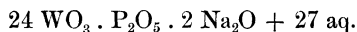


which requires:

* Berichte der deutschen chem. Gesellschaft, XIX. 823.

		Calculated.	I	II.
20 WO ₃	4640	88.85	88.75	88.84
P ₂ O ₅	142	2.73		2.74
Na ₂ O	62	1.18		1.25
21 H ₂ O	378	7.24	7.21	7.21
	<u>5222</u>	<u>100.00</u>		

The only 20 : 1 phospho-tungstate which I have hitherto described * contained 6 molecules of base (BaO), and perhaps the new salt should be written $20 \text{ WO}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{Na}_2\text{O} \cdot 5 \text{ H}_2\text{O} + 16 \text{ aq.}$ With respect to its formation with the proportions given, I may remark that I have in repeated trials failed to obtain the salt

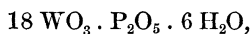


by mixing sodic tungstate and phosphate in the exact theoretical proportions and adding chlorhydric acid to the mixed solutions. The quantity of phosphate necessary to be added is much more than one molecule for twelve molecules of the tungstate. This remark appears to have been made by other chemists also.

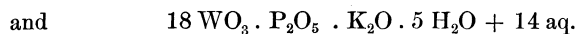
Kehrmann † has recently described phospho-tungstates which come under the general formula $18 \text{ WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3 \text{ RO}$, the salts being $18 \text{ WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3 \text{ K}_2\text{O} + 14 \text{ aq.}$, and $18 \text{ WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3 (\text{NH}_4)\text{O} + 14 \text{ aq.}$

He gives to the acid the name "Phospholuteo-wolframsäure"; but though there is little doubt that there is here a hitherto undescribed series, the analyses are not satisfactory.

In another part of this paper I have described three salts of a phosphotungstic acid which would have the formula,



the salts themselves having respectively the formulas,



These salts are however colorless, and if we admit the accuracy of Kehrmann's formulas, there must be two isomeric series. Kehrmann appears to have been wholly unacquainted with my work.

Experiments to determine the relations of WS_4K_2 , MoS_4K_2 , and $\text{WS}_2\text{O}_2\text{K}_2$, to phosphates and arsenates have not led to definite results,

* Proceedings of the American Academy, XVI. 127, and Am. Chemical Journal, II. 282.

† Zeitschrift für anorganische Chemie, IV. 138, 386.

though there seemed to be a relation of some kind. The same statement applies to the various oxyfluorides of molybdenum and tungsten.

In a communication made to the British Association * at the Montreal meeting, in 1884, I stated that complex acids existed into which platinum chloride entered, as, for instance, compounds of the type $2 \text{PtCl}_2 \cdot \text{R}_2\text{O}_3$. Since then I have made various communications on the same subject to the Harvard Chemical Club. I regard these compounds as respectively phosphoric, arsenic, and antimonie oxides, in which 2PtCl_2 replaces O_2 . A great amount of work on the subject has been done, but as it is at least possible that a very different view of the subject may be taken, I will reserve the results of my work for another occasion.

NEWPORT, R. I., August 1, 1894.

* Report for 1884, p. 670.

(*To be continued.*)